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Thermal Evidence for a Transition Above Tm in n-Alkanes and Crystalline Polymers

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SUMMARY

A series of n-alkanes, $CH_3-(CH_2)_nCH_3$, including polyethylene, crystalline polymers, and crystalline copolymers have been studied by differential scanning calorimetry at very high sensitivity through and above the melting temperature, Tm. A transition designated Tu after KRÜGER et al. is observed at about 1.2 Tm(K) (range 1.10 to 1.42). In low n-alkanes it appears as an endothermic slope change, shifting to an endothermic step change as n exceeds 100. This step change is also characteristic of polymers. Tu is rate sensitive, increasing as the rate of heating increases. Tu by DSC is higher than values reported by KRÜGER et al. from Brillouin scattering and kinematic viscosity. Tu may correspond to the temperature at which persistent structures (smectic, mesomorphic, hetical, etc.) are destroyed thermally.

INTRODUCTION

KRÜGER (1979) and KRÜGER et al. (1980) have recently presented Brillouin scattering evidence for a structural transformation in polymer melts occuring at a temperature designated Tu where Tu > Tm, the latter being the thermodynamic melting temperature. PIETRELLA and KRÜGER (1980) showed evidence for a molecular weight dependent Tu > Tm transition in the n-alkanes, using both Brillouin scattering and bulk viscosity. This latter paper has a title in the form of a question: "Are There Two Temperature Regions With Different Structure of N-Alkane Melts?" Our answer is affirmative.

We have directed attention on several prior occasions BOYER (1976a, b), (1977) to widely scattered literature presenting evidence for a transition in the melt of n-alkanes: BOTHEREL (1968), BOTHEREL and FOURCHE (1973); TANCREDE et al (1974). To these we now add BALTA-CALLEJA et al (1976). Three techniques were involved, respectively: depolarized Rayleight scattering, heats of mixing, and diamagnetic susceptibility.

In the case of crystalline polymers we cited the dilatometric studies of BECK and HILTZ (1965) on polypropylene, polybutene-1 and polypentene-1 for a transition in the 210-230°C range. None such was found for PE. They ascribed these transitions to a liquid crystal effect. SMIT (1972) presented DSC evidence for a

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T > Tm transition in i-polypropylene, ascribed to liquid crystaline structures. X-ray evidence for residual structure in the melt of i-polybutene-1 was published by BUNN (1974). ZACHMANN (1973a, b) has presented NMR evidence for transient order (lifetime 10^{-4} seconds) in the melt of PE. SNYDER and POORE (1973) have presented infrared evidence in lightly deuterated PE (140°C) suggesting that the trans-trans to gauche-gauche population is larger than that predicted by the rotational isomeric state model.

In addition to examples which we cited earlier, BOYER (1976a, b), (1977), we now add that a T > Tm transition in high cis polybutadine has been reported using internal pressure, BIANCHI and BIANCHI (1965); dilatometry, PEDEMONTE and BIANCHI (1965); and DSC, BARLOW (1978).

The effects observed for n-alkanes and crystalline polymers were, for the most part, weak, or not reproducible by others, or subject to interpretation other than that of local order, controversial and largely ignored. The findings of KRÜGER (1979), KRÜGER et al (1980) and of PIETRELLA and KRÜGER (1980) prompted us to reexamine this earlier literature. Moreover, we have recently summarized a lengthy literature and experimental study of the T > Tg liquid-liquid transition, $T_{\ell\ell}$, in amorphous polymers BOYER (1979), (1980). This too is a weak, controversial transition characterized, inter alia, by the fact that $T_{\ell\ell}(K)/Tg(K) = 1.20 \pm 0.05$ with a nominal range of 1.10 to 1.30.

While a variety of experimental techniques (dynamic mechanical, thermal, spectroscopic, and zero shear melt viscosity) showed evidence for $T_{\ell\ell}$ (BOYER, 1980), one of our prefered methods is DSC DENNY and BOYER (1981). It was, therefore, decided to investigate the DSC behaviour of n-alkanes and some semi-crystalline polymers. KRÜGER (1979) mentioned (his Ref. (14)) an unpublished DSC results on n-$C_{24}H_{50}$ by HÖHNE showing a weak transition at 100°C. No details were given, except that the strength of this transition was about 0.1% of that for Tm. Our prior experience with the weak $T_{\ell\ell}$ (about 5% of the strength of Tg) had introduced us to problems encountered at high sensitivity: namely, base line stability, instrumental noise, vibration and line voltage stability.

EXPERIMENTAL

A duPont 990-910 differential scanning calorimeter was employed in this study. The following technique was practiced: A specimen weighing 10-15 mg is used in an open DSC pan under a flowing N_2 purge. An onset temperature at least 40K below Tm is employed with an initial gain setting of 20mV/cm, a heating rate of 10K $min.^{-1}$ and a range of 10 Kcm^{-1}. Just after melting, the gain is changed to 0.5 while heating continues to ca. 150K above Tm. The combination of high sample weight with high sensitivity gain setting causes a steep endothermic slope just above Tm. This may be offset partially by using several aluminum pan lids in the reference cell, as recommended by ARNERI (1979). Initially, the specimen was cooled back to the starting temperature, examined visually for evidence of decomposition, and reheated.

However, it was immediately discovered that results could not be duplicated when reheating a once-fused specimen. BALTA-CALLEJA et al (1976) commented on the long times required for fused alkanes heated above the transition temperature to return to their initial level of diamagnetic susceptibility. We assume that nascent morphology (and/or nuclei) are destroyed on going to temperatures well above Tm. Consequently, repeat runs were always made on fresh specimens and reproducibility for both Tm and Tu was excellent.

MATERIALS USED

No characterization parameters other than melting points and Tu values are given for any of the oligomeric and polymeric materials used in this study. The polymers are mostly of common, well known structures with values of limiting Tm at high molecular weight generally available. Since we are comparing an unknown transition, Tu, to Tm, both determined by DSC, the value of Tm serves to inform whether the polymer is of low molecular weight or of normal limiting molecular weight. The polymers have come from a variety of chemical supply houses. Several sources are listed in footnotes to tables. The two Bareco^R Polywaxes, molecular wts. 1000 and 2000, are from the Bareco Division of Petrolite, Tulsa, Oklahoma.

SUMMARY OF RESULTS

Figure 1 shows typical DSC traces for the indicated n-alkanes. Three different patterns above Tm are observed with increasing values of n: 1) an endothermic slope change; 2) an endothermic peak for only C_{40}, followed by an endothermic slope change; 3) an endothermic step jump starting with Polywax 1000 and also generally seen in polymers.

Figure 2 is a DSC trace on polytetramethylene oxide to illustrate this endothermic step jump pattern. Two techniques are illustrated. In A, the high sensitivity gain setting of 0.5 is used for the entire trace. In B, the gain setting is 20 through Tm, permitting the melting peak to be recorded, followed by the higher sensitivity, 0.5, setting. It is seen that the appearance of Tu is not affected by changing the gain setting.

Tables I and II give values of Tm, Tu and Tu(K)/Tm(K) for a variety of samples. The transition values for the n-alkanes, polywaxes and Polyethylene samples discussed earlier are given in Table I. Table II consists of transition values for a variety of semi-crystalline polymers. Omitted are Tu values on high ethylene copolymers with butene and octene; and Ethylene-co-TFE. The values listed in Tables I and II represent the average of all first runs made on a particular sample. Most samples were run twice but, some were only run once while few were run 3-4 times.

DISCUSSION OF RESULTS

First of all, concerning the n-alkanes, it is impressive that Tu (or a related phenomenon) has been observed by diverse techniques with generally concordant results. These results include

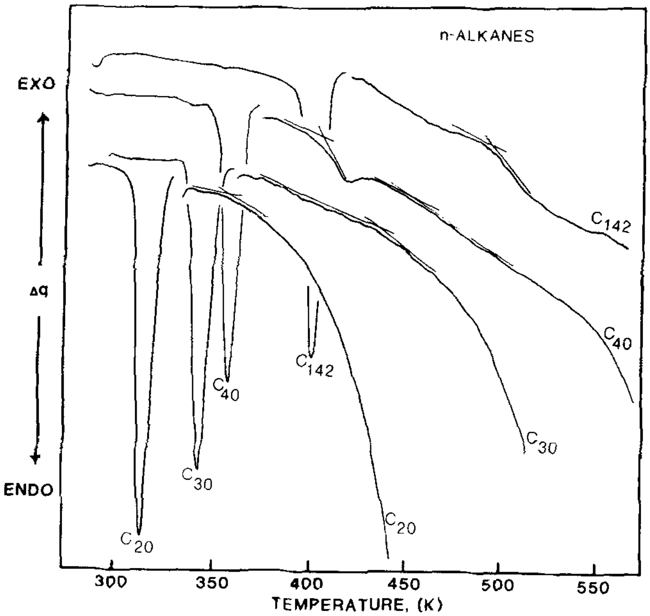

Figure 1. DSC traces for the indicated n-alkanes showing Tm at a gain setting of 20mVcm^{-1} and the T > Tu region at a gain setting of 0.5mVcm^{-1}. Tu is indicated as an endothermic peak and/or an endothermic slope change. Heating rate 10K min.$^{-1}$.

TABLE I

Tu of n-Alkanes and Polyethylene by DSC at 10K min.$^{-1}$

SAMPLE	Tm(K)	Tu(K)	Tu(K)/Tm(K)
n-Eicosane (C_{20})	313	357	1.14
n-Docosane (C_{22})	321	386	1.20
n-Tetracosane (C_{24})	328	404	1.23
n-Triacontane (C_{30})	342	434	1.27
n-Dotriacontane (C_{32})	346	430	1.24
n-Hextriacontane (C_{36})	351	435	1.24
n-Octatriacontane (C_{38})	353	467^{a}	1.32
		403^{a}	1.14
n-Tetracontane (C_{40})	356	453^{a}	1.27
		405^{a}	1.14
n-Tetra tetracontane (C_{44})	362	459	1.27
Poly-wax (C_{71}) 1000	385	485	1.26
Polywax (C_{142}) 2000	400	489	1.22^{b}
PE (NBS 1475 linear)		-	-
PE (NBS 1476 branched)	394	525	1.33
PE 6600^{c}	388	503	1.30

a) Double transition; b) see inset to Figure 3; and c) KRÜGER et al 1980 by Brillouin scattering.

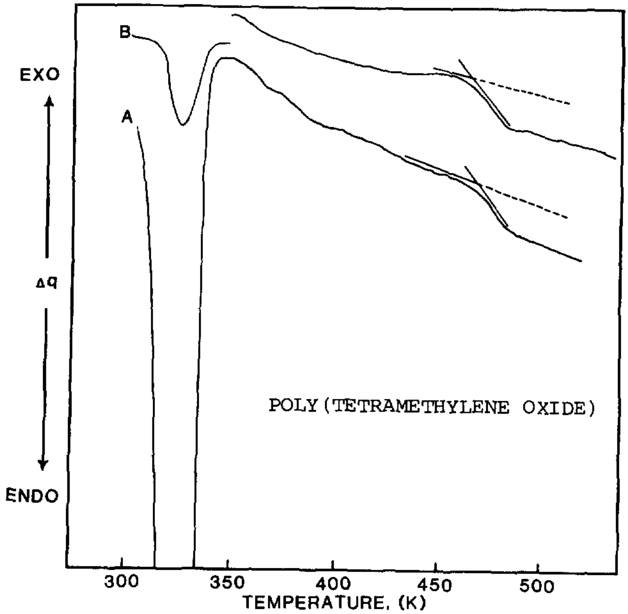

Figure 2. DSC traces for polytetramethylene oxide at 10K min.$^{-1}$. Curve A, constant gain setting of 0.5mVcm^{-1}; curve B, gain setting of 20 through Tm, 0.5 above Tm. Tu shows as the endothermic step increase.

TABLE II

Tu of Semi Crystalline Polymers by DSC at 10K min.$^{-1}$

SAMPLE	Tm(K)	Tu(K)	Tu(K)/Tm(K)
Isotactic Polypropylene	438	483	1.10
Polybutene-1	398	467	1.17
Polybutadiene high cis	273$^{a)}$	314	1.15
High trans		cross-links	
Polyethylene oxide (100,000)	340	400$^{b)}$	1.18
	340	473$^{b)}$	1.39
Polyethylene oxide 5,000$^{c)}$	339	405	1.20
Polyethylene oxide 2,000$^{c)}$	332	399	1.20
Polytetramethylene oxide$^{d)}$	327	463	1.42
Polydecamethylene oxide$^{e)}$	352	434	1.23
Polyethylene terephthalate		Decomposes	
Polybutylene - Terephthalate	499	564	1.13

a) Tm not observed on our DSC trace. 273 is a nominal value for Tm; b) Double transition; c) Monomethyle ether derivative; d) Sample courtesy of Dr. Raymond Wetton, Loughborough, England; and e) Sample courtesy of Dr. Jose Fatou, Madrid, Spain.

Brillouin scattering, kinematic viscosity, diamagnetic susceptibility and DSC. Other techniques such as depolarized light scattering and heats of mixing demonstrate some order above Tm but do not provide a transition temperature. Tu is not likely to be an artifact by all methods, although it might be by some of the techniques.

Secondly, we were surprized by the tendency for the ratio, Tu(K)/Tm(K), to cluster around 1.2, with a range of 1.10 to 1.27 except for a single high value of 1.42 for PTMO.

Perhaps even more puzzling is the fact that the above ratio and range are so similar to those for $T_{\ell\ell}$/Tg, namely, a clustering around 1.2 with a range of 1.10 to 1.30. It was suggested BOYER (1979, 1980) that this constancy for $T_{\ell\ell}$/Tg implied that $T_{\ell\ell}$ depended on the same structural factors as did Tg, mainly chain stiffness and polarity. One might speculate that Tu depends on the same factors which influence Tm. As BUNN (1955) has suggested, these are largely chain stiffness, shape and polarity, although many subtle factors play a role. We have noted BOYER (1976a) that the tendency for Tm/Tg to cluster around 1.50 is consistent with a view proposed by BUNN (1953), namely, that there is order in amorphous polymers at Tg, similar to that of crystalline polymers at Tm, but of a very local, or short range nature.

Finally, we comment, especially with regard to data in Table II, that our DSC results have received confirmation by other techniques, already alluded to in the introduction. These were the x-ray results of BUNN (1974) on polybutene-1 and the several studies on polybutadiene by Bianchi, Barlow and Pedemonte. PEDEMONTE and BIANCHI (1965) not only found a transition in high cis PBD at 55°C but also in cis-trans-vinyl copolymers of 55% cis at 37.5°C and of 32.6% cis at 37.5°C. The latter two polymers are almost certainly amorphous, thus raising the question as to a possible relationship between these PBD transitions and Tu.

Botherel has suggested (BOTHEREL ,1968) correlation of molecular orientations in the n-alkanes could well be a result of London forces which are proportional to α_ℓ^2/d^7 where α_ℓ is the polarizability and d is the intermolecular distance. The ratio is quite high in the n-alkanes as well as in the polybutadienes and polyoxides $[(CH_2)_nO]p$, which also have small intermolecular distances. BOYER and MILLER (1977) have pointed out that polymers with a small cross sectional area per chain, and hence a small intermolecular distance, exhibit high values of the Mooney-Rivlin C_2 constant. They ascribe the high C_2 to local order and strong intermolecular forces. It is possible that a transition in an amorphous cis-trans-vinyl polybutadiene could have its origin in a thermal disruption of such secondary interactions.

ASSESSMENT OF OUR n-ALKANE RESULTS

Figure 3 is a plot of DSC values for Tm and Tu from Table I plotted against 100/n. The Tm values fall on a reasonably straight line, the Tu values on the curved line as shown. We

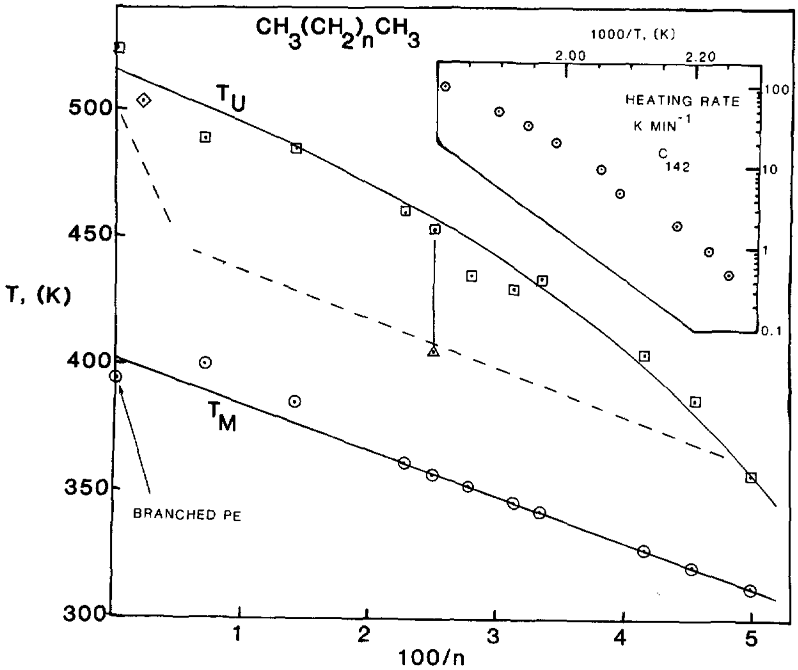

Figure 3. DSC melting points, circles, and Tu values, squares, for the indicated n-alkanes. Dashed line gives locus of Tu values KRÜGER et al, PIETRELLA and KRÜGER, and BALTA-CALLEJA et al.by several techniques. Triangle is a second Tu for C_{40} by DSC. Diamond is KRÜGER et al. Brillouin scattering value of Tu for PE 6600. Inset shows effect of DSC heating rate on Tu of polywax 2000 $\equiv C_{142}$.

were able to obtain values of Tu for various n-alkanes by the several methods: Brillouin scattering, kinematic viscosity, and diamagnetic susceptibility. Ones estimated from plotted data were slightly uncertain as to Tu or molecular weight or both. However, these values fell along the dashed line of Figure 3. Our lower transition for the C_{40} is also on this line. We ascribed the large difference between DSC and other results to the 10K min^{-1} heating rate compared with the step increases or decreases by the other methods, with a waiting period at each new temperature.

The inset to Fig. 3 shows log heating rate - 1000/T for polywax 2000. At the lowest heating rates, Tu indeed approaches the dashed line.

The other possibility involved the time effects observed by BALTA-CALLEJA et al (1976) for diamagnetic susceptibility to reach a new equilibrium value on increasing the temperature. This depends on the alkane length and the proximity to a transition but is of the order of a half hour to hours. In the case of

Brillouin and kinematic viscosity, a specimen is held for a few minutes at each successive temperature on a heating or cooling cycle.

It therefore appears that our values are high for some of the n-alkanes because of a time effect. We were naturally concerned about the possibility of an artifact in DSC studies of Tu just as we were in the case of $T_{\ell\ell}$. The availability of Tu by multiple techniques is quite reassuring. Moreover, the fact that Tu is a) molecular weight dependent; b) not seen in some polymers; and c) not seen on second heatings gave added confidence.

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ADDED NOTES. Heating rate studies on lower alkanes show same pattern as an inset to Figure 3. Long time aging at 20°C on once melted alkanes restores Tu on a second heating. Identical values of Tu were obtained with open pans and hermetically sealed pans for C_{20} and C_{44}.

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